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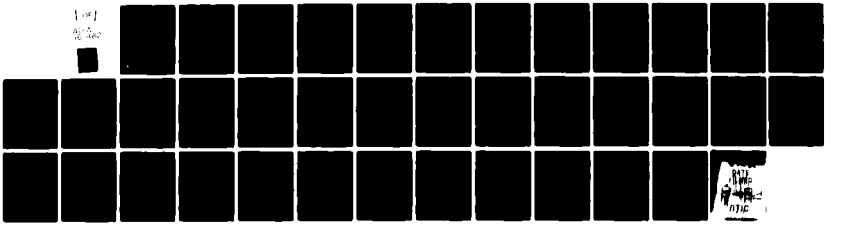

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MECHANISM OF THE REACTION BETWEEN ALKYL- AND ARYL GRIGNARD REAGENTS AND HEXACHLOROCYCLOTRIPHOSPHAZENE: AN EXPLANATION OF BI(CYCLOPHOSPHAZENE) FORMATION

by

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June 24, 1982

Mechanism of the Reaction Between Alkyl- or Aryl Grignard Reagents and Hexachlorocyclotriphosphazene: An Explanation of Bi(cyclophosphazene) Formation[1,2]

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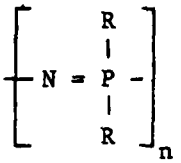
Received

Abstract: An understanding has been obtained of the complex mechanisms that are followed when alkyl- or aryl Grignard reagents react with $(NPCl_2)_3$ (2) in tetrahydrofuran. The main products are monoalkylcyclotriphosphazenes (3) and bi(cyclotriphosphazenes) (4). The predominance of one product or the other depends on the reaction temperature and on the organic functionality of the Grignard reagent. The structural characterization of the bi(cyclotriphosphazenes) is described together with the reaction pathways that lead to bi(cyclotriphosphazene) formation. Two competitive pathways exist. Nucleophilic substitution on 2 yields the monoalkylcyclotriphosphazenes (3), while metal-halogen exchange on 2, followed by chlorine replacement, generates metallophosphazene intermediate (6). Species 3 and 6 react to form the bi(cyclophosphazenes). Steric effects play a powerful role in directing the course of the reaction.

A number of major developments in the chemistry of phosphazene rings and macromolecules are hindered by the lack of knowledge about the reaction mechanisms that are followed when Main Group organometallic reagents react with halophosphazenes. Our own interest in such reactions was prompted by the growing need for new synthetic routes for the preparation of long chain poly(organophosphazenes) that contain alkyl- or aryl groups bonded to the skeleton through phosphorus-carbon bonds (1).[3,4]



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Evidence from small-molecule studies suggests that macromolecules of structure 1 should possess greater photolytic and thermal stability than conventional poly(organophosphazenes) that contain alkoxy, aryloxy, or amino groups. They would be structural analogues of the poly(organosiloxanes).

Three routes to species 1 seem promising: (1) Direct condensation synthesis from small-molecule alkyl- or arylphosphorus-silicon precursors.[5] (2) Ring-opening polymerization of alkyl- or arylcyclophosphazenes,[6] and (3) Organometallic substitutive halogen replacement reactions carried out on halogenophosphazene linear high polymers such as $(NPCl_2)_n$[7] or $(NPF_2)_n$.[3,4] The reactions discussed in this paper are relevant to routes (2) and (3), both from the viewpoint of "monomer" synthesis and as model reactions for the analogous high polymeric substitution reactions.[8]

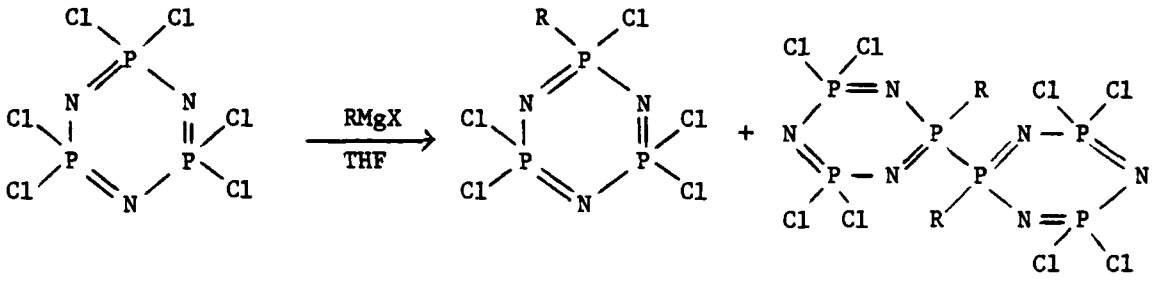
The organometallic reactions of halophosphazenes have generated considerable interest during the past decade and some controversy as well. Such reactions can result in halogen replacement by organic groups, phosphorus-nitrogen skeletal bond cleavage, or the coupling of different molecules.[9-14] (Hitherto, only traces of the last species were detected).[11,13] Previous investigators have reported that skeletal cleavage reactions predominate when $(NPCl_2)_3$ (2) reacts with phenylmagnesium bromide,[12] diphenylmagnesium[13] or phenyllithium.[14] Treatment of the macromolecular analogue, $(NPCl_2)_n$, with phenyllithium brings about appreciable skeletal cleavage.[7]

In a recent attempt to circumvent this skeletal cleavage problem, we have studied the reactions between $(NPCl_2)_3$ and alkylmagnesium chlorides in the presence of $[n\text{-}Bu_3PCuI]_4$.[15] These interactions provide access to a wide range of new alkylcyclophosphazenes without the complication of ring cleavage.[15-18] The mechanism of these processes suggested to us that the interactions of Grignard reagents alone with chlorophosphazenes might be interpreted in an entirely different way. If correct, this interpretation might allow reactions to be designed to yield species such as 1 without the complications mentioned above.

In this paper we report the surprising results obtained from a study of the reactions of alkyl- or aryl Grignard reagents with $(NPCl_2)_3$ in tetrahydrofuran. These reactions led not to ring cleavage but to the high-yield formation of two well-defined products which contained intact phosphazene rings. One of these products is a bi(cyclic) phosphazene with the two rings linked by a P-P bond.

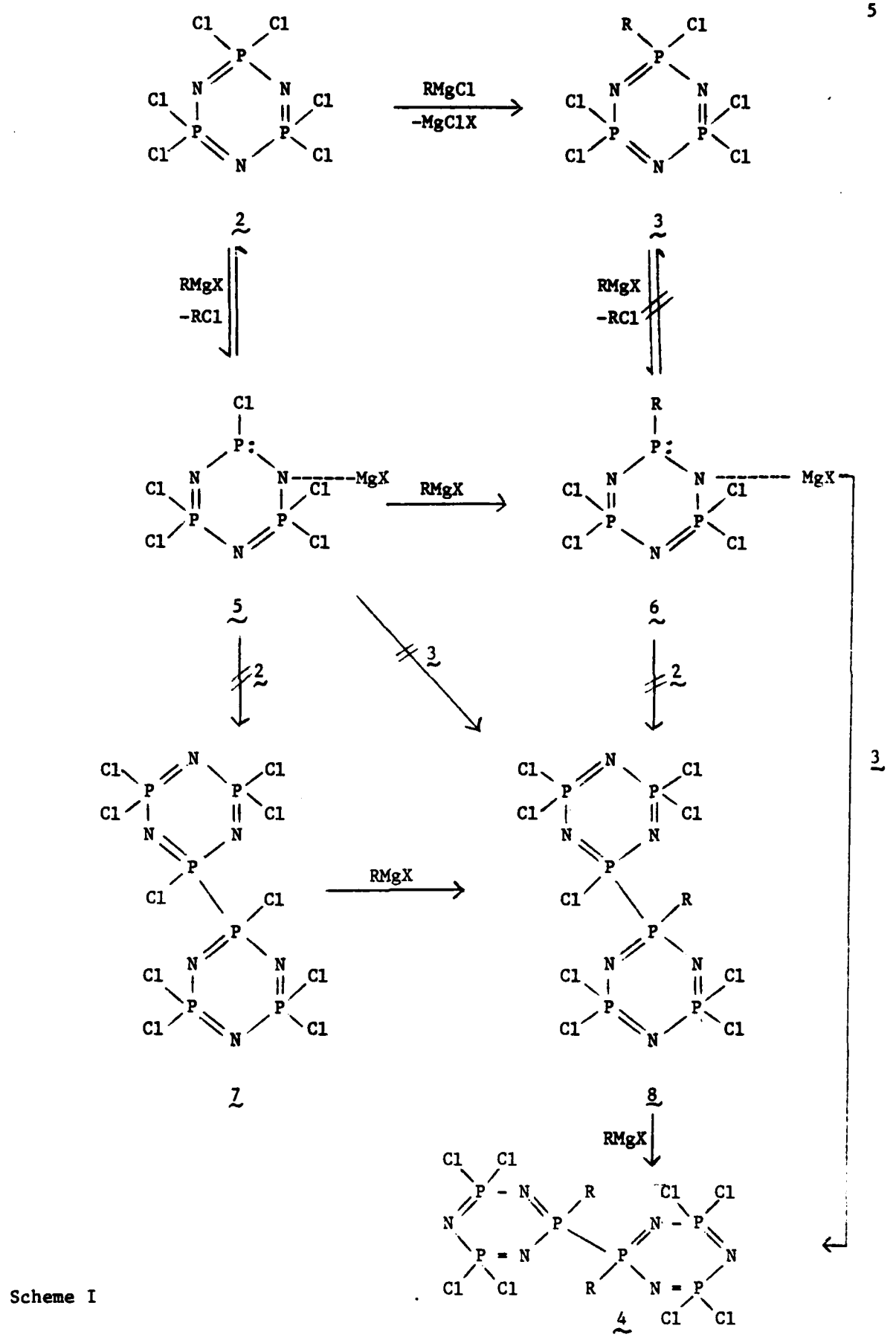
Results and Discussion

The Reaction Products. The two types of products formed when hexachlorocyclotriphosphazene (2) reacts with Grignard reagents in tetrahydrofuran in the 0°-66°C temperature range are monoalkylcyclotriphosphazenes (3) and bi(cyclotriphosphazenes) (4). Species 3 have been synthesized earlier via an alternative route.[18] They are valuable polymerization "monomers". Examples of 3 were formed in which R is CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, or t-C_4H_9.



2 3 4

However, species 4 is an unexpected product. It was obtained as a range of white, air-stable derivatives in which R is CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, or C_6H_5. The relative yields of 3 and 4 varied with the organic component of the Grignard reagent and the reaction temperature in a manner that provides clues to the reaction mechanism. The reaction conditions and yields are summarized in Table I. The structural characterization of species 4 is summarized in the Experimental section and in Tables II-IV (supplementary data).



Scheme I

Overview of the Reaction Pathway. Compounds of type 3 are apparently formed by the direct nucleophilic replacement of chlorine in 2 by the Grignard reagent (Scheme I). Similar interactions are well-documented for the reactions between cyclic fluorophosphazenes and organometallic reagents.[10,11] Moreover, it is well-known that nucleophilic displacement occurs readily when halophosphazenes react with alkoxides, aryloxides, or amines.[9]

(Scheme I near here)

The pathway that leads to the formation of the bi(cyclic) species (4) is more complex. We believe that the formation of the P-P bond is preceded by a metal-halogen exchange process to yield 5, followed by chlorine replacement which yields a metallophosphazene intermediate (6). This species then undergoes a chlorine replacement reaction with 3 to yield a bi(cyclophosphazene) (4). As shown in Scheme I, a number of additional interconnecting pathways seem plausible on theoretical grounds, but are not, in fact, followed. Later sections of this paper contain the evidence on which this statement is based.

The key assumption of the overall mechanism is the participation by metallophosphazene intermediates, such as 5 or 6. Reactive metallophosphazenes can be generated via the reactions of Grignard reagents with 2 in the presence of $[n\text{-}Bu_3PCuI]_4$,[15] and by the metallation of hydridophosphazenes.[17,28] Schmidpeter and co-workers[28] have synthesized a bi(cyclotriphosphazene) by a coupling reaction between a metallophosphazene and a halocyclophosphazene. Moreover, phosphinothioic halides react with Grignard reagents by a metal-halogen exchange pathway to yield $R_2P(S)MgX$ and an alkyl halide, followed by coupling with additional $R_2P(S)Cl$ to give

P-P bonded species.[29] Significantly, appreciable quantities of CH_3Cl or C_2H_5Cl were detected when 2 interacted with CH_3MgBr or C_2H_5MgBr.[30] The additional ethane or butane detected are indicative of a reaction between the two alkyl halides and the appropriate Grignard reagents. Thus, the evidence for the participation by metallophosphazene intermediates is quite strong, and further evidence will be developed in the following sections.

Alternative Reaction Pathways to 4. Two main reaction manifolds can be envisaged that could yield bi(cyclophosphazenes) (4). Both involve coupling reactions between a metallophosphazene and a cyclic halophosphazene. They are outlined in Scheme I. The important mechanistic questions are as follows: (1) Are the final reaction products (4) generated via 7 or by the more complicated routes that involve 3 or 6? (2) Is the mono-organo-cyclotriphosphazene product (3) a reaction intermediate on the pathway to 8 or 4, or is it a non-participating side product? (3) Do these reactions involve free radical or ionic processes? As shown in Scheme I, one rather complex pathway that does involve 3 appears to be responsible for the formation of bi(cyclophosphazenes). The evidence for this pathway (and against the alternative routes) is summarized in the following sections.

^{31}P NMR Analysis of the Reaction. The involvement of monoalkyl-cyclotriphosphazenes (3) in the formation of bi(cyclophosphazenes) (4) was detected by a monitoring of the progress of the reaction using ^{31}P NMR spectroscopy. In a typical experiment, 0.5 equivalent of Grignard reagent (relative to $(NPCl_2)_3$) was added to a THF solution of 2 at 0° or 66°C. The solution was then stirred for 24 h and an aliquot was analyzed by ^{31}P NMR spectroscopy.[20] The procedure was then repeated until the starting material (2) could no longer be detected or until 2.0 equivalents of Grignard reagent had been added.

When 2 was treated with C_2H_5-, n-C_3H_7-, or n-C_4H_9MgX at 0°C, species 3 was detected first. As compound 4 began to appear, the concentration of 3 increased to a maximum and then decreased. By the point at which all the starting material (2) had been consumed, the concentration of 4 had exceeded that of 3. This behavior is illustrated in Figure 1 for the reaction of n-C_4H_9MgCl with $(NPCl_2)_3$ at 0°C. Similar results were obtained when all three reactions were carried out at 66°C. Methylmagnesium halides gave rise to similar behavior except that the concentration of 3 was significantly less than in the other three cases. Also, species 4 constituted the only product present by the time that 2.0 equivalents of Grignard reagent had been added at 0°C.

The results described above demonstrate that compounds of type 3 must participate as reaction intermediates in the pathway that leads ultimately to 4. If the two types of compounds were formed by independent mechanisms, no decrease in the concentration of either product would be observed. The data also suggest that $N_3P_3Cl_5CH_3$ is more reactive to ring-coupling reactions than are $N_3P_3Cl_5C_2H_5$, $N_3P_3Cl_5C_3H_7$-n, or $N_3P_3Cl_5C_4H_9$-n.

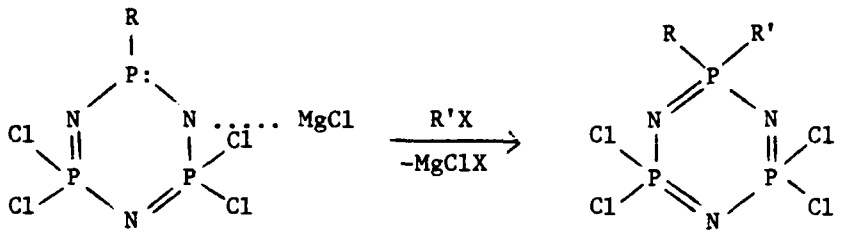
Species 3 could not be detected when the Grignard reagent was C_6H_5MgX. The bi(cyclic) compound (4) was the only product detected throughout the reaction. By contrast, i-C_3H_7MgCl or t-C_4H_9MgCl generated species 3 only -- no bi(cyclic) compounds at all were formed. These differences will be discussed later.

Influence of the Schlenk Equilibrium. Why does the product ratio depend on the amount of Grignard reagent added? One explanation is based on changes in the Schlenk equilibrium. Grignard reagents are essentially monomeric in tetrahydrofuran, but they do participate in the Schlenk equilibrium (eq. a) in this medium.[31]

$$R_2Mg + MgCl_2 \rightleftharpoons 2RMgCl \qquad (a)$$

Magnesium chloride is a product of the halogen-replacement reaction which yields 3. Hence, equilibrium (a) may be moved to the right as the formation of 3 continues. Suppose that one of the species, R_2Mg or RMgCl, is responsible for the nucleophilic substitution that converts 2 to 3, and that the other reagent is involved mainly with the ring-coupling reaction that yields 4. Under these circumstances the preponderance of 3 or 4 in the reaction mixture would depend on the total amount of Grignard added. This may be a contributing factor, but it does not explain all the experimental data. For example, it does not account for the decline in the concentration of 3 as 4 is formed in the later stages of the reaction. Furthermore, the yields of 3 and 4 were unaffected when added $MgCl_2$ (saturated solution) was present during the reactions of CH_3-, C_2H_5-, n-C_4H_9-, i-C_3H_7, or C_6H_5MgCl with 2 at 0°C. Thus, changes in the Schlenk equilibrium probably exert only a minor influence on the course of the reaction. A more plausible explanation involves the nature of the intermediates in the reaction sequence.

Nature of the Metallophosphazene Intermediate. If metallophosphazenes, such as 5 or 6, are intermediates in the reaction sequence, it should be possible to "trap" them by reaction with a reactive alkyl halide. Species 5 would yield a monoalkylcyclotriphosphazene (3), and intermediate 6 should yield a 1,1-dialkyl-3,3,5,5-tetrachlorocyclotriphosphazene (9).



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The addition of 2 equivalents of alkyl- or arylmagnesium halide to a mixture of $(NPCl_2)_3$ and iodomethane in tetrahydrofuran at 0°C yielded mainly the 1,1-methylalkyl- or 1,1-methylaryl-derivatives (9).[32] The yields from these reactions are listed in Table V. The presence of iodomethane reduced the yield of the bi(cyclic) product (4). Only very low yields of 4 were obtained when CH_3MgCl or C_6H_5MgCl were used, and 4 was entirely absent when n-C_4H_9MgCl was employed. Thus, the evidence favors the view that species 6 lies on the main pathway from 2 to 4. However, it does not eliminate the possibility that intermediate 5 lies on the same pathway. Of course, species 3 (R=CH_3) is formed along with 9 when 2 reacts with CH_3MgCl in the presence of CH_3I, but this simply reflects the nucleophilic displacement reaction.[33] Thus, the question remains of whether 6 is formed from 3 or from 5, and this will be discussed in a later section.

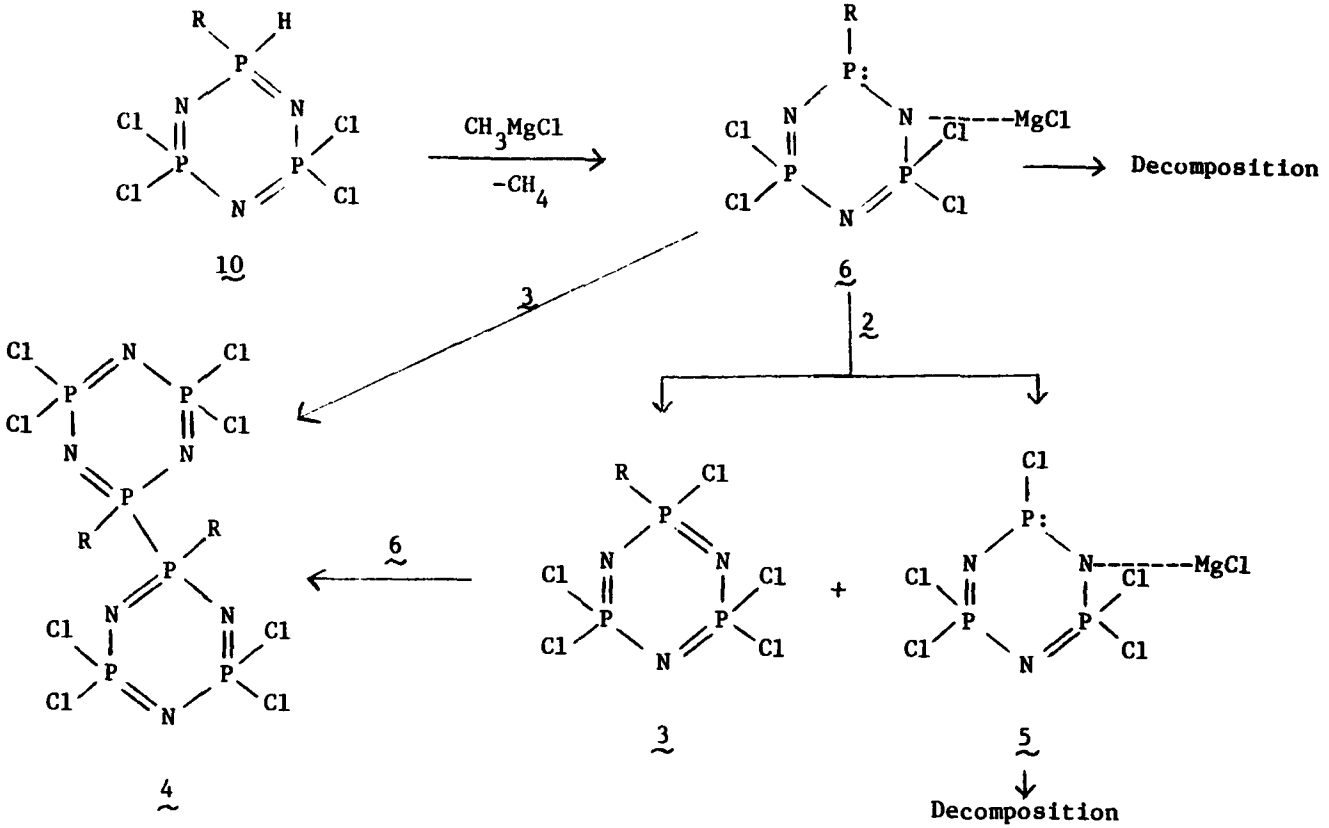
Compounds 9 were formed even when secondary or tertiary alkylmagnesium halides were allowed to react with 2 in the presence of iodomethane. This indicated that sterically hindered Grignard reagents can undergo the metal-halogen exchange process. Thus, the inability of the system to yield bi(cyclotriphosphazenes) with i-propyl and t-butyl Grignard reagents is

due to steric hindrance at the ring-coupling stage and not at the point of metallophosphazene formation. The formation of $N_3P_3Cl_4(CH_3)_2$ from the reaction of 2 with t-C_4H_9MgCl in the presence of iodomethane reflects the presence of CH_3MgCl generated via metal-halogen exchange between t-C_4H_9MgCl and CH_3I.

Route for the Formation of Metallophosphazene 6. As mentioned earlier, two plausible reaction pathways can be envisaged for the formation of 6. Intermediate 6 could be formed from 2 via a metal-halogen exchange reaction that involves species 3 or through a halogen-replacement reaction that involves the (unidentified) metallophosphazene intermediate 5. Though less likely on theoretical grounds, it appears that 6 is formed from 5 rather than from 3 (Scheme I). Treatment of $N_3P_3Cl_5CH_3$ with 1 equivalent of RMgCl in tetrahydrofuran at 0°C yielded species of type 9 by alkyl- or aryl-halogen replacement.[32] Compounds of type 4 were not detected. This is consistent with the activation of molecules such as 3 to geminal nucleophilic halogen replacement by alkoxides, aryloxides, or amines.[18]

The Ring-Coupling Reaction. If, as appears to be the case, metallophosphazene 6 lies on the principal pathway to 4, two alternative ring-coupling steps are possible. Species 6 could react with $(NPCl_2)_3$ (2) to yield 8, which would then react with Grignard reagent to give 4. Alternatively, 6 might react with 3 to form 4 directly (Scheme I).

First, it is probably significant that no bi(cyclic) intermediates such as 7 or 8 were isolated or detected from these reactions, even though they would be expected to be quite stable in the absence of excess Grignard.



Scheme II

This fact alone would argue against the participation of $(NPCl_2)_3$ (2) in the main ring coupling steps.

Second, the observation that the concentration of 3 first rises and then falls as the reaction to 4 proceeds, suggests that 3 reacts with 6 to form 4.

Third, it was possible to prepare metallophosphazene 6 by treatment of the hydridocyclotriphosphazene, $N_3P_3Cl_4(R)H$ (10), with CH_3MgCl[17] (Scheme II).

(Scheme II near here)

The interaction of 6 with 3 (where R = CH_3, C_2H_5, or C_6H_5) brought about a high-yield conversion to 4 (Table VI). The ease with which the phenyl derivative of 3 reacts with 6 may explain why this product was never detected in the original reactions. However, no ring-coupling occurred when the group R in 3 was i-C_3H_7 or t-C_4H_9. On the other hand, no species of type 8 were detected when 6 reacted with $(NPCl_2)_3$ (2).[34] The only products found were 3 and 4. Species 3 was formed presumably by chlorine abstraction from 2 by 6 (Scheme II). Such halogen-abstraction processes are known when $(NPCl_2)_3$ reacts with organo-transition metal anions.[35] However, this provides a less efficient route to 4 than does the reaction of 6 with 3 (Table IV). Species such as 6 or 5 are known to be unstable above -60°C.[17] Because the route to 4 via 2 (Scheme II) involves a greater risk of decomposition of a metallophosphazene (roughly twice the risk), the loss of cyclotriphosphazene rings is correspondingly greater by this route.[36]

Explanation of Product Distribution. Two competitive pathways exist when $(NPCl_2)_3$ reacts with Grignard reagents. These are nucleophilic substitution or metal-halogen exchange. Metal-halogen exchange reactions

are often favored over substitution at low temperatures. As shown in Table I, this is found to be the case because bi(cyclo) derivatives (4) are favored over mono-organocyclotriphosphazenes (3) at the lower temperatures.

The ability of a metallophosphazene (6) and a cyclotriphosphazene of type 3 to ring-couple should diminish as the substituent group, R, becomes larger. In practice, higher yields of 4 are obtained when R is CH_3 rather than C_2H_5, n-C_3H_7, or n-C_4H_9 (Table I). Secondary and tertiary alkyl groups completely inhibit P-P bond formation. Even the nucleophilic substitution reaction that leads to 3 is sensitive to steric constraints. For example, only a 50% conversion of $(NPCl_2)_3$ to $N_3P_3Cl_5C_4H_9$-t took place in the presence of 2 equivalents of Grignard reagent at 66°C. The factors which control ring-coupling when R is C_6H_5 are less clear, but are most likely electronic in nature.

The proposed mechanism is also consistent with the reaction stoichiometry. Four equivalents of Grignard reagent are consumed per two phosphazene rings in the formation of 4. One equivalent is used to generate 3, one is consumed in metallation to yield 5, one for halogen replacement to give 6, and up to one equivalent for reaction with the liberated alkyl halide to generate R-R. Thus, in terms of the observed facts, two equivalents of CH_3MgX are required for the complete consumption of 2, but only one equivalent of i-C_3H_7MgCl is needed (Table I). Those reactions that yield similar proportions of 3 and 4 (where R = C_2H_5, n-C_3H_7, and n-C_4H_9) consume 1.5 equivalents of organometallic reagent.

These results provide clues to what might be expected when high polymeric $(NPCl_2)_n$ reacts with Grignard reagents. The formation of P-P

bonds would generate crosslinks which would be detrimental to complete halogen replacement. Thus, the design of reaction conditions that favor substitution over metal-halogen exchange is a key requirement for macromolecular synthesis. However, it is known[37] that P-P bonds can be cleaved by alkoxides and aryloxides, and this may provide a route for the introduction of both alkyl or aryl and alkoxy or aryloxy side groups into the macromolecular system.

Experimental Section.

Materials. Hexachlorocyclotriphosphazene (2) was supplied by Ethyl Corp. and was purified by sublimation followed by two recrystallizations from n-hexane. The Grignard reagents were obtained commercially from Alfa-Ventron as 1.5-3.0 M solutions in tetrahydrofuran or diethyl ether. These were analyzed before use by the method of Watson and Eastham[38] using 2,2'-biquinoline as an indicator. Tetrahydrofuran (THF) (Baker) was distilled into the reaction flask under an atmosphere of dry nitrogen from a sodium-benzophenone ketyl drying agent. Anhydrous magnesium chloride (Aldrich) was dried for several days in vacuo at 160-170°C. Iodomethane (Aldrich) was distilled from P_2O_5 before use. Alkyl and aryl substituted phosphazenes, $N_3P_3Cl_4(R)H$ and $N_3P_3Cl_5R$ were prepared using procedures described elsewhere.[15,18,39] All manipulations involving air-sensitive reagents or substrates were carried out either in a nitrogen-filled glove box equipped with a recirculating system to remove oxygen and water, or with the use of typical Schlenk-tube techniques.

Reactions of Grignard reagents with $(NPCl_2)_3$. A solution of $(NPCl_2)_3$, 2, (5.0 g, 0.014 mol) in THF (140 mL) was either cooled to 0°C or heated to

reflux, (66°C). The Grignard reagent (see Table I), dissolved in either THF or diethyl ether, was added dropwise to the solution. After every 0.5 equivalent of Grignard reagent per $(NPCl_2)_3$ had been added, the addition was stopped and the solution was stirred for 60 min. At the end of this time, a further 0.5 equivalent of the Grignard reagent was added, and the procedure was repeated until all the reagent had been added. The reaction mixture was then stirred for 24 h. A 2 mL aliquot of the mixture was then transferred via syringe into a nitrogen-filled NMR tube and was analyzed.[20] The data obtained are listed in Table I.[19]

Isolation of the Bi(cyclotriphosphazenes). After an aliquot from the reactions described above had been analyzed by ^{31}P NMR spectroscopy, the reaction products were isolated in the following manner. The solvent was removed under reduced pressure and the products were extracted with dichloromethane. The solution was then filtered through a silica gel column (4 cm x 8 cm) to remove traces of magnesium halides. Biphenyl (obtained from the reaction of 2 with C_6H_5MgX) was removed by washing with hot hexane (2 x 200 mL). Separation of compounds 3 and 4 was achieved by gradient elution through a silica gel chromatography column with C_6H_{14}/CH_2Cl_2 solvent. The bi(cyclotriphosphazenes) were further purified by recrystallization from C_6H_{14}/CH_2Cl_2 media. The yields of compounds 4 ranged from 39-75% (Table II).

Isolation of Gaseous Products. To a solution of $(NPCl_2)_3$ in THF at 66°C was added either methyl- or ethylmagnesium bromide as described above. A stream of nitrogen was passed over the reaction mixture, through a trap cooled to -196°C (500 mL) and through an oil "bubbler". When the addition

of the Grignard reagent was complete, the solution was refluxed for 8 h. At the end of this time, the cold trap was evacuated, allowed to warm to 25°C, and backfilled with nitrogen. Samples of the gaseous mixture were withdrawn from the collection vessel and subjected to gas chromatography/mass spectrometric analysis.[30] Chloromethane and ethane were detected when CH_3MgBr was used, while the reaction with C_2H_5MgBr yielded chloroethane and butane.

^{31}P NMR Monitoring. The reactions between Grignard reagents and $(NPCl_2)_3$ at 0° or 66°C were carried out as described above with the following modifications. After 0.5 equivalent of the Grignard reagent per $(NPCl_2)_3$ had been added, the addition was stopped and the solution was stirred for 24 h. At the end of this time, a 2 mL aliquot of the reaction mixture was transferred via syringe into a nitrogen-filled NMR tube and was analyzed.[20] A further 0.5 equivalent of the Grignard reagent was then added and the procedure was repeated until either the starting material (2) could no longer be detected or 2.0 equivalents of Grignard reagent had been added. The data presented in Figure 1 were obtained by analysis of the reaction mixture following the reaction of successive 0.25 equivalent of n-C_4H_9MgCl.

Reactions between Grignard Reagents and $(NPCl_2)_3$ in $MgCl_2$-Saturated THF. A solution of $(NPCl_2)_3$ (5.0 g, 0.014 mol) and $MgCl_2$ (4.0 g, 0.42 mol) in THF (140 mL) was cooled to 0°C. The Grignard reagent (see Table I), dissolved in THF or diethyl ether, was added dropwise to the solution. After every 0.5 equivalent of Grignard reagent per $(NPCl_2)_3$ had been added, the addition was stopped and the solution was stirred for 60 min. At the end of this time, a further 0.5 equivalent of the Grignard reagent was added and the

procedure was repeated until all the reagent had been added. The reaction mixture was then stirred for 24 h. At the end of this time, a 2 mL aliquot of the solution was transferred via syringe into a nitrogen-filled NMR tube and was analyzed.[20] The reaction was carried out using methyl-, ethyl-, n-butyl-, i-propyl-, and phenylmagnesium chloride. In each case the composition of the product mixture was identical to that listed in Table I.

Metallophosphazene Trapping Reactions. A solution of $(NPCl_2)_3$ (2.5 g, 0.007 mol) and iodomethane (0.44 mL, 0.007 mol) in tetrahydrofuran (70 mL) was cooled to 0°C. The Grignard reagent (0.014 mol), dissolved in THF or diethyl ether, was then added dropwise to the solution. Two types of Grignard addition were employed.[33] In the first (slow addition), 0.5 equivalent of Grignard reagent was added. The solution was then stirred for 24 h. At the end of this time, a 2 mL aliquot of the reaction mixture was transferred by syringe into a nitrogen-filled NMR tube and was analyzed.[20] A further 0.5 equivalent of the Grignard reagent was then added, and the procedure was repeated until all of the reagent solution had been added. The results obtained are listed in Table V. Alternatively, the entire 2.0 equivalents of Grignard reagent were added over a period of 15 min (fast addition). The solution was stirred for 24 h. After this time a 2 mL aliquot of the reaction mixture was transferred via syringe into a nitrogen-filled NMR tube and was analyzed. These results are also listed in Table V.

Reactions of Grignard Reagents with $N_3P_3Cl_5CH_3$. A solution of $N_3P_3Cl_5CH_3$ (1.0 g, 0.003 mol) in THF (30 mL) was cooled to 0°C. The Grignard reagent (0.003 mol), dissolved in THF, was then added dropwise

to the solution. After 0.5 equivalent of the Grignard reagent had been added, the addition was stopped and the solution was stirred for 60 min. At the end of this time, the remaining 0.5 equivalent of Grignard reagent was added and the solution was stirred for 24 h. A 2 mL aliquot of the reaction mixture was then transferred via syringe into a nitrogen-filled NMR tube and analyzed.[20,40]

Metallation of $N_3P_3Cl_4(R)H$ in the Presence of $N_3P_3Cl_5Y$. All of these reactions were carried out in an identical manner. The following procedure is typical: A solution of $N_3P_3Cl_4(CH_3)H$ (1.0 g, 0.003 mol) and $N_3P_3Cl_5CH_3$ (1.1 g, 0.003 mol) in THF (30 mL) was cooled to 0°C. A solution of CH_3MgCl (1.05 mL, 2.9 M) in THF was then added dropwise over a period of 15 min. The solution was then stirred for 24 h. At the end of this time, a 2 mL aliquot of the reaction mixture was transferred via syringe into a nitrogen-filled NMR tube and was analyzed.[20] The data obtained are listed in Table VI.[19] The cyclic products were then recovered in the following manner: The solvent was removed under reduced pressure and the products were extracted with CH_2Cl_2. This solution was then filtered through a silica gel column (2 cm x 4 cm) to yield 1.4 g of cyclic products (70% based on starting material used).

Reaction of $N_3P_3Cl_4(CH_3)H$ with CH_3MgCl. A solution of $N_3P_3Cl_4(CH_3)H$ (1.0 g, 0.003 mol) in THF was cooled to 0°C. A solution of CH_3MgCl (1.05 mL, 2.9 M) in THF was added dropwise over a period of 15 min. The solution was stirred for 24 h. At the end of this time, a 2 mL aliquot of the reaction mixture was transferred into a nitrogen-filled NMR tube and was analyzed. Phosphazene compounds, $N_3P_3Cl_5CH_3$ and $[N_3P_3Cl_4CH_3]_2$, were detected along with other unidentified products. The solvent was then removed under

reduced pressure and the products were extracted with CH_2Cl_2. This solution was filtered through a silica gel column (2 cm x 4 cm) to yield 0.05 g of 3 and 4.

Proof of Structure of Compounds 4. The bi(cyclotriphosphazenes) synthesized in this study were characterized by infrared spectroscopy, ^1H and ^{31}P NMR spectroscopy, mass spectrometry (low and high resolution) and, in a representative case, elemental analysis.[22] These data are listed in Tables II-IV (Supplementary Material). Moreover, the structures of the methyl[41] and phenyl[42] derivatives have been confirmed by single-crystal X-ray structure determinations.

The mass spectral data[21] for compounds 4 are listed in Table II. All the compounds yielded a weak parent ion in the mass spectrum, with a characteristic Cl_8 isotope pattern. The most abundant ions (Cl_4 isotope pattern) corresponded to fragments resulting from cleavage of the P-P bond.[11,13]

The infrared spectra[23] of compounds 4, listed in Table III, were consistent with the proposed structures. In each case an intense absorbance between 1100 and 1300 cm^{-1} was observed. This is characteristic of the PN skeleton of cyclic phosphazene compounds.[9] Other bands in these spectra were tentatively assigned to C-H and P-Cl absorbances. The Raman spectra of compounds 4 (R = CH_3 and C_6H_5) have also been recorded.[37]

The proton-decoupled ^{31}P NMR spectra (listed in Table IV) of the bi-(cyclotriphosphazenes) were interpreted as $M_2AA'M'_2$ spin systems.[24,26,37] The resonance assigned to the nuclei constituting the P-P linkage appeared at 17.7 ppm (R = C_6H_5) or between 26.4 and 31.9 ppm (R = alkyl). The other resonance in the spectrum, assigned to the PCl_2 group, appeared at ≈20 ppm. These assignments were confirmed from the proton undecoupled ^{31}P NMR spectrum

in which the former resonance broadened due to unresolved proton-phosphorus coupling. The latter resonance remained virtually unchanged.

The organic side groups in compounds 4 were identified by inspection of the high field ^{1}H NMR spectra of these compounds.[25] These data are also listed in Table IV. Due to the various complex proton-phosphorus coupling interactions, only a limited number of coupling constants could be determined readily.[27] However, a detailed interpretation of ^{1}H NMR couplings for bi(cyclotriphosphazenes) has recently been presented.[37]

Acknowledgments. We thank the U.S. Office of Naval Research for the support of this work. We also thank R. A. Nissan for obtaining high field NMR spectra and P. R. Suszko for the GC/MS data.

Supplementary Material Available. Tables II-IV for bi(cyclotriphosphazenes) showing mass spectral and elemental analysis data (Table II), infrared data (Table III), and ^{31}P NMR and ^{1}H NMR data (Table IV). Ordering information is given on any current masthead page.

References and Notes

1. This paper is Part in a series on phosphorus-nitrogen ring systems and high polymers. For a previous paper in this series see:

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19. Percentages are based on relative proportions of phosphazene rings.

20. Relative yields were determined from integrated ^{31}P NMR spectra of crude reaction mixtures using a Varian Associates CFT-20 spectrometer operating at 32 MHz. The flip angle employed in the FT data collection was 45° and the pulse repetition rate was 30 sec. Acquisition of 500-600 scans was required to give well-resolved spectra. The peak integrations were accurate to less than ±3%.

21. Electron impact mass spectral data were obtained with the use of an AEI MS 902 mass spectrometer.

22. Elemental analysis was obtained by Galbraith Laboratories, Knoxville, TN. 37921.

23. Infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrometer. The samples were prepared as KBr disks.

24. ^{31}P NMR spectra were recorded with the use of a Bruker WP-200 spectrometer operating at 80 MHz or a Varian Associates CFT-20 spectrometer operating at 32 MHz. All spectra were obtained for solutions of the compounds in $CDCl_3$. Positive chemical shifts are downfield from external phosphoric acid.

25. ^{1}H NMR spectra were recorded with the use of a Bruker WP-200 spectrometer operating at 200 MHz. All spectra were obtained on a solution of the compound in $CDCl_3$. Chemical shifts are relative to tetramethylsilane at $\delta = 0$.

26. No phosphorus-phosphorus couplings were observed for the alkyl-substituted bi(cyclotriphosphazenes). However, fine splitting was observed in the proton decoupled ^{31}P NMR spectrum of 4 (R = C_6H_5) when it was obtained at 80 MHz employing a Gaussian multiplication with -5.0 Hz line broadening, $|J_{PNP} + J_{PPNP}| = 8.7$ Hz.

27. No attempts were made to determine the absolute sign of any of the coupling constants.

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32. Species of type 9 have been prepared by alternative routes.[16]

33. Initially, reactions between Grignard reagents and 2 in the presence of CH_3I were monitored by ^{31}P NMR spectroscopy following the addition of 0.5 equiv. of organometallic reagent (see Experimental section). This procedure was used in order to determine if phosphazene compounds other than those detected in the final reaction mixture were present at earlier stages. None were observed. When the entire 2 equiv. of Grignard were added during the first 15 min of the reaction, slightly higher yields of 9 were obtained. This is because the side reaction between RMgCl and CH_3I is minimized by rapid addition of the Grignard reagent.

34. A further confirmation of the proposed pathway is provided by the fact that, when R in 10 and 6 is C_2H_5 or C_6H_5, no methyl derivatives of 3 or 4 are formed. Hence, the Grignard reagent used to convert 10 to 6 does not participate further in the reaction.

35. Allcock, H. R.; Riding, G. H. unpublished observations.

36. The formation of 6 from 10 (R = CH_3) in the absence of 2 or 3 generated traces of 3 (R = CH_3) or 4 (R = CH_3), but most of the product did not contain cyclotriphosphazene rings.

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39. Compounds analogous to 3, 9, and 10 in which R = C_6H_5 have recently been prepared: Allcock, H. R.; Connolly, M. S., manuscript in preparation.

40. Percent conversions[19,20] to 9 were as follows: R = R' = CH_3, 69%; R = CH_3, R' = n-C_4H_9, 65%; R = CH_3, R' = C_6H_5, 47%.

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Table I. Reactions of Alkyl and Aryl Grignard Reagents with $(NPCl_2)_3$ in Tetrahydrofuran.[19,20]

Grignard Reagent	React. Temp. (°C)	%3	%4	Equiv. $RMgX/(NPCl_2)_3$
CH_3MgCl[a]	0	0	100	2.0
CH_3MgCl[a]	66	15	85	2.0
CH_3MgBr[b]	0	0	100	2.0
CH_3MgBr[b]	66	17	83	2.0
C_2H_5MgCl[a]	0	47	53	1.5
C_2H_5MgCl[a]	66	62	38	1.5
C_2H_5MgBr[b]	0	46	54	1.5
C_2H_5MgBr[b]	66	64	36	1.5
$\underline{n}$-C_3H_7MgCl[a]	0	46	54	1.5
$\underline{n}$-C_3H_7MgCl[a]	66	64	36	1.5
$\underline{n}$-C_4H_9MgCl[a]	0	47	53	1.5
$\underline{n}$-C_4H_9MgCl[a]	66	69	31	1.5
$\underline{i}$-C_3H_7MgCl[b]	0	100	0	1.0
$\underline{i}$-C_3H_7MgCl[b]	66	100	0	1.0
$\underline{t}$-C_4H_9MgCl[a]	0	very slow reaction[c]		2.0
$\underline{t}$-C_4H_9MgCl[a]	66	50[d]	0	2.0
C_6H_5MgCl[a]	0	0	100	2.0
C_6H_5MgCl[a]	66	0	100	2.0
C_6H_5MgBr[b]	0	0	100	2.0
C_6H_5MgBr[b]	66	0	100	2.0

[a] Grignard reagent in THF. [b] Grignard reagent in diethyl ether. [c] No reaction observed after 48 h. [d] Remainder of phosphorus-containing compounds consisted of unreacted $(NPCl_2)_3$.

Table V. Reactions of Alkyl and Aryl Grignard Reagents with $(NPCl_2)_3$ in the Presence of Iodomethane.[a,19,20]

Grignard Reagent	Rate of Addition[b]	%9	%3	%4	%2
CH_3MgCl	slow	39	4	5	52
CH_3MgCl	fast	46	3	5	46
n-C_4H_9MgCl	slow	59	13	0	28
n-C_4H_9MgCl	fast	75	5	0	20
i-C_3H_7MgCl	slow	94	6	0	0
i-C_3H_7MgCl	fast	100	0	0	0
t-C_4H_9MgCl[c]	slow	17	0	0	62
t-C_4H_9MgCl[d]	fast	17	0	0	65
C_6H_5MgCl	slow	30	0	17	53
C_6H_5MgCl	fast	35	0	12	53

[a] Two equivalents of Grignard reagent were added to an equimolar mixture of $(NPCl_2)_3$ and CH_3I in THF at 0°C. [b] See Experimental section. [c] 1,1-Dimethylcyclotriphosphazene (21%) was also observed, [d] 1,1-Dimethylcyclotriphosphazene (18%) was also observed.

Table VI. Metallation of Hydridophosphazenes in the Presence of a Halophosphazene.[a,19,20]

$N_3P_3Cl_4(R)H$	$N_3P_3Cl_5Y$	%4	%3	%2	% Cyclic Prods. Recvd.[b]
R = CH_3	Y = CH_3	92	8	-	70
R = CH_3	Y = Cl	16	26	58	55
R = C_2H_5	Y = C_2H_5	53	47	-	73
R = C_2H_5	Y = Cl	5	25	70	57
R = $\underline{i}$-C_3H_7	Y = $\underline{i}$-C_3H_7	0	100	-	48
R = $\underline{i}$-C_3H_7	Y = Cl	0	40	60	47
R = $\underline{t}$-C_4H_9	Y = $\underline{t}$-C_4H_9	0	100	-	47
R = $\underline{t}$-C_4H_9	Y = Cl	0	37	63	45
R = C_6H_5	Y = C_6H_5	100	0	-	72
R = C_6H_5	Y = Cl	59	0	41	58

[a] One equivalent of CH_3MgCl was added to an equimolar mixture of $N_3P_3Cl_4(R)H$ and $N_3P_3Cl_5Y$ in THF at 0°C. [b] Based on amounts of cyclic starting materials employed.

Figure 1. Changes in the relative concentrations of phosphazene compounds as n-C_4H_9MgCl is added to $(NPCl_2)_3$ at 0°C in THF (● $(NPCl_2)_3$; ▲ $N_3P_3Cl_5$n-C_4H_9; ■ $[N_3P_3Cl_4$n-$C_4H_9]_2$).[19,20]

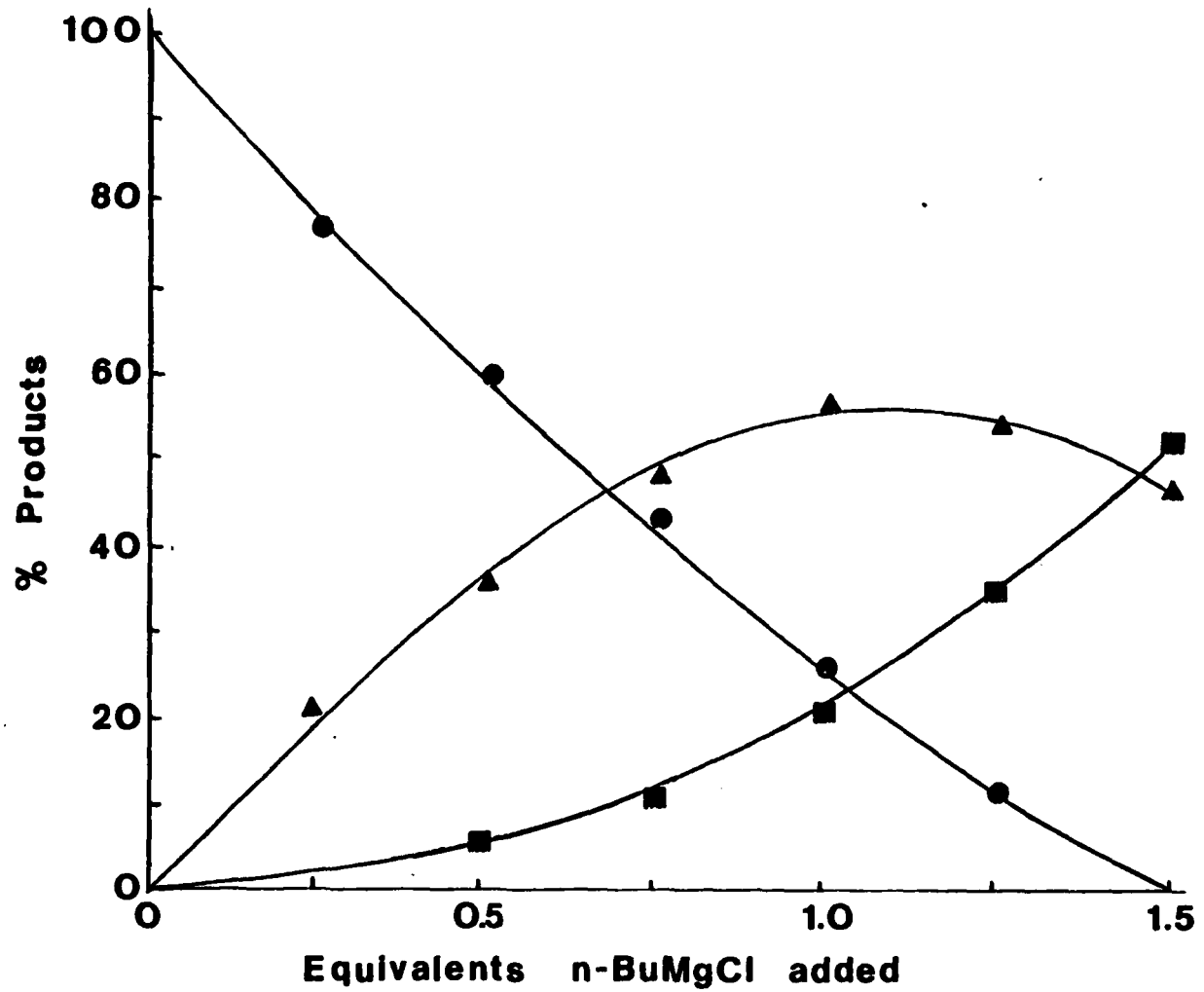
100
80
60
40
20
0
% Products
0
0.5
1.0
1.5
Equivalents n-BuMgCl added

Table II. Bi(cyclotriphosphazene) Characterization Data.

Compound	% Yield[a]	m.p. (°C)	Mass spectral data[21] found	calc.	Elemental anal.[21,22] found	calc.
$[N_3P_3Cl_4CH_3]_2$	75	205	580	580	C 4.18	4.11
					H 1.10	1.02
					N 14.02	14.39
					P 31.89	31.85
					Cl 48.57	48.60
$[N_3P_3Cl_4C_2H_5]_2$	41	187	608	608	607.6912	607.6900
$[N_3P_3Cl_4\underline{n}\text{-}C_3H_7]_2$	43	206	636	636	635.7225	635.7213
$[N_3P_3Cl_4\underline{n}\text{-}C_4H_9]_2$	39	129	664	664	663.7556	663.7527
$[N_3P_3Cl_4C_6H_5]_2$	60	249	704	704	703.6924	703.6900

[a] Isolated yield from reaction of RMgCl with $(NPCl_2)_3$ in THF at 0°C.

Supplementary Material

Table III. Bi(cyclotriphosphazenes) Infrared Data.[23]

Compound	C-H	P-N	P-Cl
$[N_3P_3Cl_4CH_3]_2$	2970 (w)	1280 (m)	590 (s)
	2870 (w)	1170 (s)	555 (s)
	1390 (w)	1120 (sh)	
$[N_3P_3Cl_4C_2H_5]_2$	2970 (w)	1260 (m)	580 (s)
	2930 (w)	1230 (sh)	510 (s)
	2900 (w)	1180 (s)	
	1450 (w)		
	1395 (w)		
$[N_3P_3Cl_4\underline{n}\text{-}C_3H_7]_2$	2960 (w)	1230 (s)	580 (s)
	2920 (w)	1170 (s)	510 (s)
	2870 (w)		
	1460 (w)		
	1390 (w)		
$[N_3P_3Cl_4\underline{n}\text{-}C_4H_9]_2$	2955 (w)	1225 (m)	580 (s)
	2930 (w)	1200 (sh)	515 (s)
	2870 (w)	1175 (s)	
	1460 (w)		
	1395 (w)		
$[N_3P_3Cl_4C_6H_5]_2$	3050 (w)	1180 (s)	575 (s)
		1115 (m)	510 (s)

Supplementary Material

Table IV. Bi(cyclotriphosphazene) NMR Data

Compound	^{31}P NMR Data (ppm)[24] PPR	PCl_2	^1H NMR Data (δ)[25]		Coupling Constants[26,27] (Hz)
$[N_3P_3Cl_4CH_3]_2$	26.4	19.8	$-C\underline{H}_3$	1.90 (m)	unresolved
$[N_3P_3Cl_4C_2H_5]_2$	31.9	20.4	$-C\underline{H}_2CH_3$	2.00 (m)	unresolved
			$-CH_2C\underline{H}_3$	1.29 (m)	$J_{HCCH} = 7.1$
$[N_3P_3Cl_4\underline{n}\text{-}C_3H_7]_2$	30.0	20.1	$-C\underline{H}_2CH_2CH_3$	1.94 (m)	unresolved
			$-CH_2C\underline{H}_2CH_3$	1.75 (m)	unresolved
			$-CH_2CH_2C\underline{H}_3$	1.11 (t)	$J_{HCCH} = 7.0$
$[N_3P_3Cl_4\underline{n}\text{-}C_4H_9]_2$	30.5	20.0	$-C\underline{H}_2CH_2CH_2CH_3$	1.96 (m)	unresolved
			$-CH_2C\underline{H}_2CH_2CH_3$	1.68 (m)	unresolved
			$-CH_2CH_2C\underline{H}_2CH_3$	1.51 (m)	unresolved
			$-CH_2CH_2CH_2C\underline{H}_3$	0.94 (t)	$J_{HCCH} = 7.0$
$[N_3P_3Cl_4C_6H_5]_2$	17.7	19.8			$\lvert J_{PNP} + J_{PPNP} \rvert = 8.7$
			$-C_6\underline{H}_5$	7.70 (m)	unresolved

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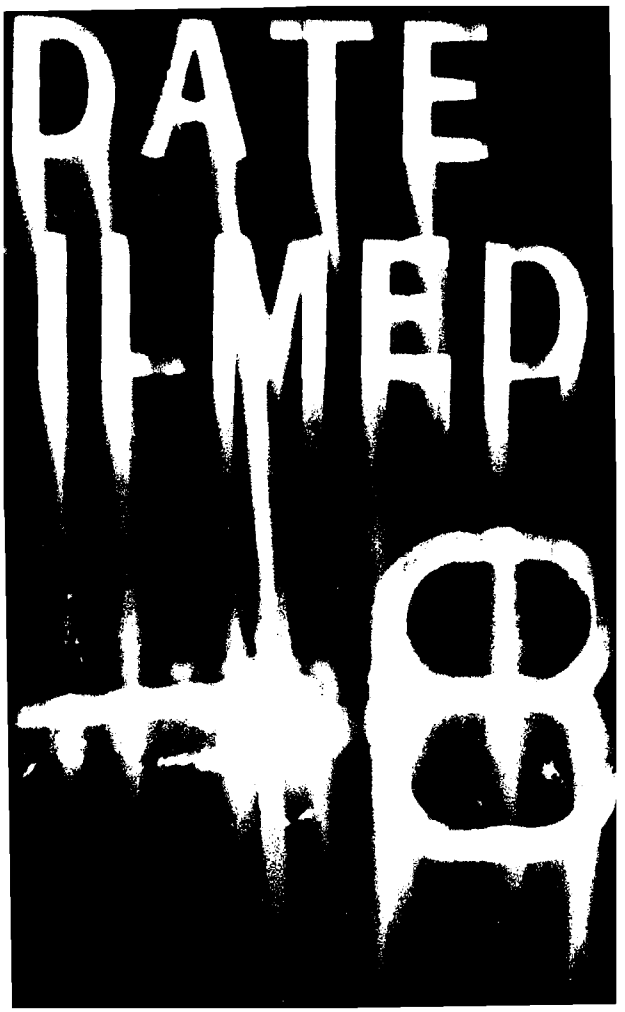
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